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Ordering in self-organizing comb copolymer-like systems obtained by hydrogen bonding between charged or noncharged polymers and amphiphiles

O. Ikkala [a,*], J. Ruokolainen [a], M. Torkkeli [b], J. Tanner [a], R. Serimaa [b], G. ten Brinke [a,c,1]

[a] *Department of Engineering Physics and Mathematics, Helsinki University of Technology, PO Box 2200, FIN-02015 HUT, Espoo, Finland*

[b] *Department of Physics, University of Helsinki, PO Box 9, FIN-00014, Helsinki, Finland*

[c] *Department of Polymer Science and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Abstract

Mesomorphic structures and order–disorder transitions in comb copolymer-like systems obtained by hydrogen bonding of noncharged or charged homopolymers with amphiphiles are discussed. The amphiphiles consist of attractive and repulsive moieties and the emphasis will be on the situation without an additional solvent phase. Poly(4-vinyl pyridine), i.e. P4VP, hydrogen bonded to stoichiometric amounts of pentadecylphenol (PDP) is one of the characteristic examples. Small angle X-ray scattering and dynamic rheology demonstrate that this system forms a disordered melt at temperatures above the order-disorder temperature (T_{ODT}), whereas for $T < T_{ODT}$ a lamellar microphase separated structure is observed. Further cooling renders side chain crystallization. This phase behavior can be tailored by adjusting the attraction and the repulsion between the amphiphile and the polymer. Repulsion can be increased by making the alkyl chain longer or by adding charges to the backbone. Both lead in general to a higher T_{ODT}. Order-disorder transitions can occur even in polyelectrolyte-amphiphile complexes as is demonstrated by first fully complexing P4VP with toluene sulphonic acid (TSA) to form a polymeric salt P4VP(TSA)$_{1.0}$ which is further hydrogen bonded to PDP. The presented results offer guidelines to apply the concepts to other polymers as well, with an example mentioned in relation to polyamide 6.

Keywords: Polymer; Amphiphile; Hydrogen bonding; Specific interaction; Microphase separation; Order-disorder transition; Block copolymer

1. Introduction

In the context of polymer-surfactant interactions (on the extensive literature see, for example, [1–4] and the references therein) the conditions to

* Corresponding author.

[1] G. ten Brinke can also be contacted with regards to this paper.

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achieve micellar-like structures are usually considered in the presence of an additional solvent phase, even if the latter is not explicitly mentioned. The most important case is the aqueous solution where the hydrophilic and hydrophobic interactions provide the driving forces for structure formation. Here we take a different starting point, more closely related to the conventional microphase separation of block copolymers (for a review, see [5]) with no separate solvent phase. It is well known that mixing of homopolymers usually leads to macrophase separation due to vanishing entropy of mixing combined with unfavourable interactions. However, if such 'repulsive' homopolymers are connected to form block copolymers of various architectures, they may form microphase separated structures. Lamellar, cylindrical, spherical and more complicated bicontinuous morphologies, some of which are only metastable, have been reported [5]. As a function of temperature, an order-disorder transition may take place. This transition can be observed most easily by small angle scattering and rheological measurements [5]. At this point, one may appreciate the close conceptual analogy between aqueous polymer-surfactant systems (structure formation due to the hydrophobic-hydrophilic competition) and block copolymers (structure formation due to a balance between attractive and repulsive interactions between the blocks). In the conventional block copolymers the attractive interaction between the repulsive blocks is permanent, i.e. chemical.

Based on such considerations, we decided to investigate whether block copolymer-like microphase separated structures and order-disorder transitions can still be achieved even if the repulsive blocks are bonded together only due to various nonpermanent, i.e. physical interactions. Such an alternative procedure could be challenging both for scientific and technical reasons: (1) Polymerization of well defined conventional block copolymers may not be straightforward in all cases to acquire systematically tailored properties and block lengths. Consequently, it is appealing to consider whether the two 'blocks' could be synthesized separately, each at their optimal conditions, and let to interact only afterwards to form block copolymer-like physically bonded complexes. Several aspects of mesomorphic structures of complexes between flexible polymers and surfactants, or more generally end-functionalized oligomers, have been presented during recent years [6–24]. (2) Selforganization of polymeric complexes is interesting even in its own right, as is also suggested in biochemistry. (3) Novel applications may be achieved, such as the selforganized structures of electrically conducting polymers leading to processibility [25,26] and conducting blends with common polymers [27].

Here we describe mesomorphic structures of comb copolymer-like molecules, which are obtained by hydrogen bonding amphiphiles to polymers and discuss the corresponding order-disorder transitions. As a background we first review our results on mesomorphic structures of noncharged polymers hydrogen bonded to amphiphiles [17–20] and then present our latest results on order-disorder transitions of charged polymers (polyelectrolytes) hydrogen bonded to amphiphiles in a more complicated manner. Here amphiphiles refer to compounds containing a group having an attractive interaction with the polar polymer, in addition to a nonpolar repulsive alkyl tail. Small angle X-ray scattering (SAXS) and dynamic rheometry data related to the order-disorder transitions will be presented. It will be discussed how to tailor the phase behavior by modifying the attraction [19] (by selecting attractive interactions of different strengths) and repulsion (by modifying the length of the alkyl tail of the amphiphile or by adjusting the polarity of the polymer by introducing charges). This latter aspect is of very recent date and very intriguing. Finally it must be pointed out that several types of 'matching' attractive interactions can be used: examples are provided by charge transfer [15] and coordination complexation [16], but also more complicated sterically tailored combinations, i.e. molecular recognition, have been demonstrated in selected cases [26].

2. Experimental

2.1. Materials

Atactic poly(4-vinyl pyridine), i.e. P4VP, with a viscosity averaged molecular weight $M_v = 49\,000$ g mol^{-1} is used as a model polymer. P4VP was acquired from Polysciences and it was used without further purification. P4VP is versatile for the present investigations because it allows hydrogen bonding (the nitrogen of the pyridine ring being a hydrogen bonding acceptor), coordination complexation (due to the lone electron pair of the nitrogen), and charge transfer (due to possibility for acid/base interactions). Therefore, many types and strengths of attractive interactions with the amphiphiles can be systematically investigated.

3-*n*-Pentadecylphenol (PDP), i.e. 3-*n*-$C_{15}H_{31}$–C_6H_4–OH, with a purity of 97% has been acquired from Pfaltz and Bauer and was used without purification. 4-*n*-Nonadecylphenol (NDP), i.e. 4-*n*-$C_{19}H_{39}$–C_6H_4–OH, was synthesized from 1-bromooctadecane and 4-methoxybenzaldehyde using the conventional Grignard reaction, and the intermediate product 1-(4-methoxyphenyl)-1-nonadecanol was reduced with hydriodic acid and red phosphorus [28]. The structure of the resulting 4-*n*-Nonadecylphenol was identified by mass spectroscopy and FTIR. Laboratory purity dodecyl benzene sulphonic acid (DBSA) was acquired from Tokyo Kasei. Its zinc salt, i.e., $Zn(DBS)_2$ was prepared using anhydrous ethanol from ZnO and DBSA [16]. In all cases the alkyl tails constitute the repulsive tail and its length can be used to tailor the extent of repulsion.

The materials were first dried in vacuum at 60°C at least for 1 day. The polymer-amphiphile complexes were prepared by dissolving the compounds in an analysis grade common solvent (DMF, chloroform or methanol which were dried using 3Å molecular sieves). The solvent was first evaporated using a hot plate at mild heating and the final drying was performed at 60°C in vacuum for ca. 2 days. The dried polymer-amphiphile complexes have been stored in a dessicator. More details can be found elsewhere [16,17,19,20].

2.2. Characterization

Time resolved SAXS was performed using fine focus Cu X-ray tube in a point focusing mode. The Cu K_α radiation was monochromatized using a Ni filter and totally reflecting glass block. The scattered radiation was detected by a one dimensional proportional counter (MBraun OED-50M). The samples could be heated using a Linkham microscope hot stage. More details can be found elsewhere [16,17,19,20].

Part of the SAXS measurements were performed at beamline 8.2 of Synchrotron Radiation Source in Daresbury, UK. For additional details, see [18,29]. Additional samples have been measured at the DESY/HASYLAB synchrotron source in Hamburg, Germany, using the Polymer Beamline.

The dynamic storage and loss moduli $G'(\omega)$ and $G''(\omega)$ were measured at different temperatures using Bohlin VOR controlled strain rheometer in the frequency range from 0.01 to 20 Hz. The geometry constitutes a fixed inner cylinder with a diameter of 14 mm, cone angle 15° and an oscillating outer cylinder of diameter of 15.4 mm [20].

3. Results and discussion

3.1. Mesomorphic phases of noncharged polymers due to hydrogen bonded amphiphiles

Pentadecylphenol (PDP) is an illustrative example of an amphiphile that is able to perform a strong hydrogen bond to P4VP [17,19]. The phenol group is slightly acidic (pK_a ca. 10) and therefore it acts as a hydrogen bonding donor for P4VP whose nitrogens are hydrogen bonding acceptors. Different mole fractions x of PDP are used versus 1 mole of vinyl pyridine repeat unit to prepare the complexes P4VP(PDP)$_x$. Accordingly, $x = 1.0$ corresponds to the nominally fully complexed case where every pyridine ring has been complexed using an amphiphile. The free and hydrogen bonded pyridine groups have their characteristic FTIR absorption bands that allow to study the actual degree of the complexation versus

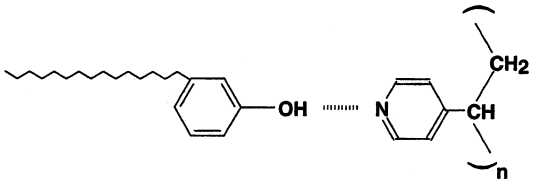

Fig. 1. Hydrogen bonding between P4VP and PDP.

the nominal amount of PDP. That the hydrogen bonding is nearly complete for $x = 1.0$ was thus confirmed [17]. Fig. 1 shows the resulting hydrogen bonded complex.

Typical SAXS patterns as a function of temperature are shown in Fig. 2 using P4VP(PDP)$_{0.7}$. At sufficiently high temperature in the melt state (at 100°C, for example) the material is disordered with only a broad SAXS peak of a low intensity. It is due to block copolymer-like concentration fluctuations [30,31]. Cooling at 5°C min^{-1} results in a strongly increased intensity and reduced width of the SAXS peak at the order–disorder transition to a lamellar phase at T_{ODT} ca. 62°C [18] (a schematical illustration of the phases is presented in the insets of Fig. 3). Further cooling yields crystallization of the pentadecyl side chains at T_c ca. 10°C. Such a time resolved SAXS behaviour at ODT is analogical with block copolymers [5]. As another method, measuring the viscoelastic behavior has become one of the most frequently used methods to identify order–disorder transitions in block copolymers [5]. In our case, dynamic rheometry was performed using the sample P4VP(PDP)$_{1.0}$ to corroborate the SAXS findings [20]: At $T > T_{ODT}$, the dynamic storage and loss moduli behave as $G' \sim \omega^{1.5}$ and $G'' \sim \omega$. Note that $G' \sim \omega^2$ and $G'' \sim \omega$ would be expected for disordered homopolymer melt. The difference in G' reflects more subtle effects produced by fluctuations in the disordered phase [5]. Passing T_{ODT} during the cooling renders $G' \approx G'' \sim \omega^{0.5}$ characteristic for lamellar morphologies in conventional block copolymer melts. Further cooling beyond T_c renders solid like behavior as is expected for crystalline solid, i.e. $G' \sim \omega^0$. Therefore, block copolymer-like behaviour is observed even in dynamic rheology.

Fig. 3 shows the phase diagram of P4VP(PDP)$_x$. For small amounts of PDP ($x \leq 1.0$), all of the above three phases are observable.

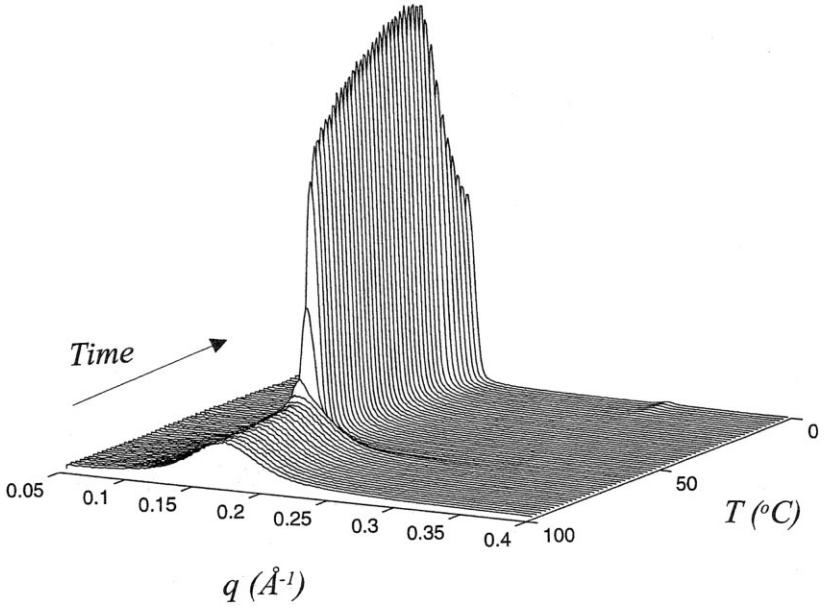

Fig. 2. Time resolved SAXS intensity curves for P4VP(PDP)$_{0.7}$ during cooling at 5°C min^{-1}, showing $T_{ODT} \approx 62$ and $T_c \approx 10$°C. The data has been collected at Daresbury.

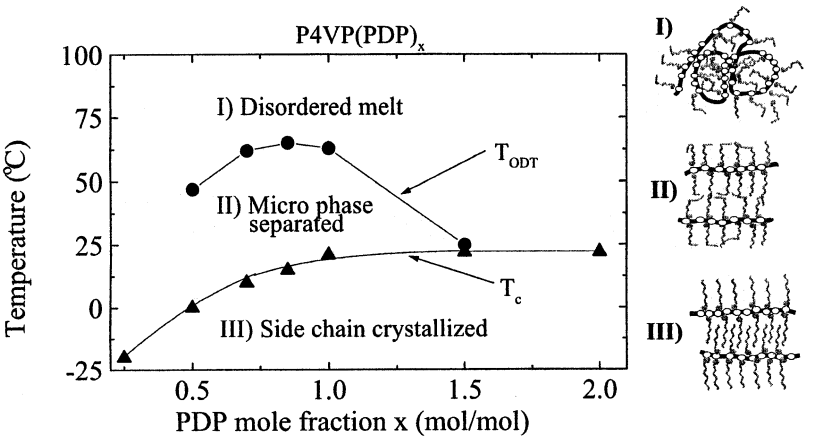

Fig. 3. Phase behavior of P4VP(PDP)$_x$ showing the order–disorder temperatures to the lamellar phase (T_{ODT}) and crystallization temperatures (T_c) of the $C_{15}H_{31}$-side chains of pentadecylphenol.

For large x ($\gg 1$), the microphase separation is no longer observed and indications for macrophase separation have been observed [20].

One can next ask what are the precise conditions for achieving microphase separated structures and how to influence the order–disorder temperatures. We will illustrate the possibilities by modifying the above P4VP(PDP)$_x$ complexes. Firstly, the phenyl group of the alkyl phenol is removed to provide aliphatic alkyl alcohols. They are essentially nonacidic (pK_a ca. 15–17) and, therefore, they are significantly less effective hydrogen bonding donors, as also demonstrated using FTIR [19]. Thus, it is no surprise that, for example, hexadecanol simply macrophase separates from P4VP because the repulsion due to the long alkyl tail overcomes the poor attractive hydrogen bonding [19]. Therefore, one of the essential ingredients to achieve mesomorphic structures in polymer–amphiphile complexes is to have sufficiently strong attraction.

The above example also demonstrates that the repulsion between the alkyl tail and the polar polymer backbone plays an important role. The effect will be further illustrated by two examples which also demonstrate the 'tunability' of the system: Firstly, stronger repulsion can be induced simply by increasing the length of the alkyl tail of the alkyl phenol. For that purpose, complexes with nonadecylphenol (NDP) were prepared, i.e. P4VP(NDP)$_x$. Mesomorphic phases are observed even in this case, which confirms that the strength of the hydrogen bond suffices to balance the increased repulsion. However, even the relatively small increase in the alkyl chain length of only four methyl units induces a large increase in T_{ODT}. For example, in the case of the nominally fully complexed samples P4VP(C_nH_{2n+1}–C_6H_4–OH)$_{1.0}$, $T_{ODT} \approx 63$°C for $n = 15$ during cooling (at 5°C min^{-1}) whereas $T_{ODT} \approx 95$°C for $n = 19$ during cooling (at 20°C min^{-1}). This is in agreement with the expectation that a larger repulsion will result in an increased T_{ODT}.

Secondly, for fixed alkyl tails, the repulsion can be increased by adding charges to the polymeric backbone or to the polar part of the amphiphile. Selected examples will be discussed in the next section.

3.2. Mesomorphic phases of charged polymers due to hydrogen bonded amphiphiles

The effect of added charges in P4VP(PDP)$_x$ can be studied by noting that the pyridine nitrogens of P4VP can first be quaternized using sulphonic acids R–SO_3H, as well as other strong acids. This scheme will be illustrated using toluene sulphonic acid (TSA), i.e., CH_3–C_6H_4–SO_3H. Due to the quaternization, the polymer backbone becomes charged poly(4-vinyl pyridinium toluene

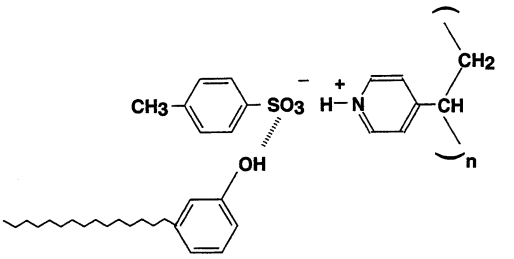

Fig. 4. Suggested hydrogen bonding between $P4VP(TSA)_{1.0}$ and $(PDP)_{1.0}$. Toluene sulfonic acid (TSA) is bonded to the pyridine ring due to quaternization whereas pentadecylphenol (PDP) is suggested to be hydrogen bonded to the sulphonate anion.

sulphonate), as confirmed by the characteristic FTIR absorption band 1637 cm^{-1} of the resulting pyridinium rings. The sulphonate groups, in turn, are expected to be hydrogen bonding acceptors, suggesting hydrogen bonding with PDP. Direct spectroscopic evidence of such hydrogen bonding is still lacking but there are indirect arguments suggesting its feasibility: In $P4VP(TSA)_{1.0}$ complexed with various amounts of PDP to form $P4VP(TSA)_{1.0}(PDP)_x$, the characteristic pyridinium FTIR absorption band at 1637 cm^{-1} is observed at all temperatures used in this work, showing that the formation of salt between P4VP and TSA is relatively stable. In this polysalt the most feasible site of the hydrogen bonding is expected to be the sulphonate groups. A scheme of the potential $P4VP(TSA)_{1.0}(PDP)_x$ complexes is shown in Fig. 4. In this work we limit the discussion to the case where nominally all of the pyridine rings are converted to pyridinium rings and only the mole fraction of PDP is allowed to vary, in analogy with Section 3.1. In this case, nominally each repeat unit of the polymer backbone is charged.

SAXS data collected during slow heating at 3°C min^{-1} are shown in Fig. 5 for $P4VP(TSA)_{1.0}(PDP)_{0.75}$. The results resemble the scattering data described for $P4VP(PDP)_x$ (Figs. 2 and 6), showing a sharp and distinct SAXS peak due to mesomorphic phase for $T < T_{ODT}$ and a disordered phase with a correlation hole peak for $T > T_{ODT}$. However, the magnitude of the T_{ODT} has increased from ca. 62 up to ca. 228°C upon additional complexation due to toluene sulphonic acid. A in this respect similar situation is encountered if methane sulphonic acid (MSA), i.e. $CH_3–SO_3H$, is used in which case $T_{ODT} \approx 100$°C. In that case, however, the system exhibits a much

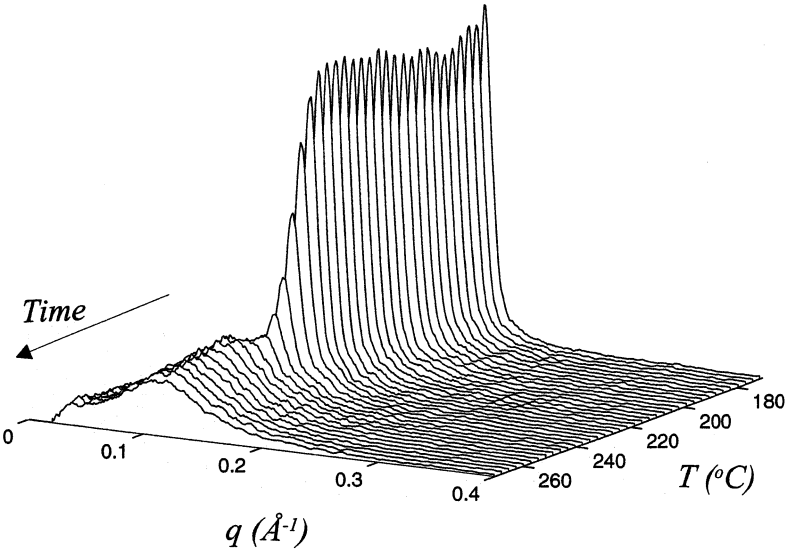

Fig. 5. Time resolved SAXS of $P4VP(TSA)_{1.0}(PDP)_{0.75}$ during a slow heating at 3°C min^{-1}, showing the $T_{ODT} \approx 228$°C. The data has been collected using a conventional X-ray source.

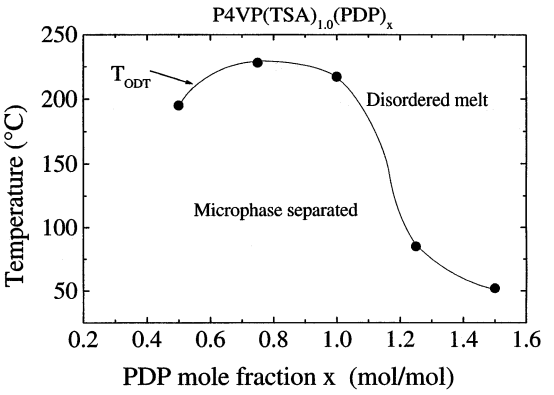

Fig. 6. Order–disorder transitions of $P4VP(TSA)_{1.0}(PDP)_x$ as a function of the PDP mole fraction.

more complex phase behavior including re-entrant phase behavior (closed loop phase boundaries), which is discussed elsewhere [39]. With respect to the issues addressed here, one can conclude that complexing different moieties to the polymer backbone using quaternization is a very effective method to influence (increase) T_{ODT}. Also the actual structure of the counter-ion has an effect.

Note that previously different types of mesomorphic structures of polyelectrolyte-surfactant complexes have been reported in the literature [6–12,15,32] but order–disorder transitions were not presented, to our knowledge, if the components are nonmesogenic.

There are also other related structures involving charges: Zn^{2+} and selected other metal cations are known to form strong complexes with the nitrogens of the pyridine group. Therefore it is not astonishing that, for example, $Zn(DBS)_2$ forms mesomorphic complexes with P4VP [16]. The generality of these concepts can be demonstrated also by mesomorphic structures of polyamide 6 complexed with $Zn(DBS)_2$ [21]. Finally, as already stated, amphiphilic strong acids may form strong bonding to P4VP due to quaternization. In the case of P4VP, mesomorphic complexes can thus be obtained by complexing, for example, dodecyl benzene sulphonic acid (DBSA) [15]. Investigations on possible order–disorder phenomena in the latter two cases are still in progress.

4. Conclusions

Sufficiently strong physical interactions between a polymer and an amphiphile allow mesomorphic structures to be formed by the polymeric complexes. The phase behavior can be tailored by balancing the competing attractive and repulsive interactions using different types of attractive interactions, different lengths of the alkyl tail, and charges. Hydrogen bonded polymer-amphiphile complexes were shown to behave in many respects like comb copolymers: mesomorphic phases and order–disorder transitions are observed. But, due to the dynamic nature of the bonding, potentially a much more rich phase behavior may occur, including re-entrant phases and other macrophase separated phases [24,39]. Here we mentioned explicitly only lamellar phases, but it has been shown that a rich variety of morphologies is possible [11].

The above-mentioned polymeric comb copolymer-like complexes can also be regarded as a special case of molecular bottle-brushes [23,33,34] where the 'brushes' are dynamically bonded. If an additional solvent phase is introduced, we approach systems traditionally studied in colloidal science. If one starts from a pure P4VP- amphihile system and gradually adds a good solvent for the alkyl side chains, mesomorphic phases may be expected to persist during the dilution process until the complexes cease to overlap. For example, $P4VP(DBSA)_{1.0}$ remains mesomorphic still when more than 50%-wt xylene is added [15]. In extremely dilute solution, another interesting question arises whether an isolated bottlebrush can be sufficiently extended due to the excluded volume effect between the side chains to form a nematic solution. Theoretically, this question has been answered both affirmatively as well as negatively [35,36]. Recent Monte-Carlo calculation seem to indicate (at least within the limit of the present simulation capacity) that liquid crystallinity cannot be induced by increasing the stiffness of the structure by simply increasing the side chain length. Rather, the simulations seem to suggest that the actual topology of the side groups, such as their size, may be a more important factor [37,38].

The route to form block copolymer-like structures using physical interactions opens possibilities to prepare tailored microstructures combining the expertise obtained in block copolymers and colloidal systems.

Acknowledgements

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